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(21) International Application Number: PCT/SE00/00237 (22) International Filing Date: 8 February 2000 (08.02.00) (30) Priority Data: 9900605-8 19 February 1999 (19.02.99) SE (71) Applicant (for all designated States except US): ABB ATOM AB [SE/SE]; S-723 63 Västerås (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): ABR Y, Philippe [FR/SE]; Haga Parkgata 6E, S-723 36 Västerås (SE). BORELL, Sten [SE/SE]; Drivisvägen 4, S-722 31 Västerås (SE). ERIKSSON, Sven [SE/SE]; Mäster Jacobs väg 28, S-730 50 Västerås (SE). (74) Agents: BJERKÉN, Håkan et al.; Bjerkéns Patentbyrå KB, P.O. Box 1274, S-801 37 Gävle (SE).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. In English translation (filed in Swedish).</i>
(54) Title: A METHOD FOR PRODUCTION OF AND MATERIAL ADAPTED TO BE SINTERED TO A NUCLEAR FUEL ELEMENT WITH OXIDE BASE		
(57) Abstract A method for production of a nuclear fuel element with oxide base, in which the nuclear fuel with oxide base is mixed with Cr and sintered to a solid body. The amount of chrome oxide added is ≥ 50 and < 1000 ppm with the respect to the amount of nuclear fuel with oxide base added.		

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A method for production of and material adapted to be sintered to a nuclear fuel element with oxide base

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BACKGROUND OF THE INVENTION AND PRIOR ART

The present invention related to a method for production of a nuclear fuel element with oxide base, in which the nuclear fuel with oxide base is mixed with chrome oxide and sintered into a solid body. The invention also relates to a material with oxide base adapted to be sintered to a nuclear fuel element, which comprises a nuclear fuel with oxide base and chrome oxide.

Methods and materials of the type mentioned above are already known within the field of nuclear energy applications. The nuclear fuel with oxide base may comprise UO_2 , ThO_2 , PuO_2 or a mixture thereof, and is provided as powder.

Different editions of further oxides, such as TiO_2 , Nb_2O_5 , Cr_2O_3 , Al_2O_3 , V_2O_5 and MgO have according to the prior art been added to the nuclear fuel with oxide base for obtaining an increase of the grain size thereof in connection with the sintering thereof, since said additions activate the crystalline growth of the grains of the nuclear fuel during the sintering.

The increased grain size results in a need of a longer time for gas enclosures in the grains to diffuse to grain boundaries and through these out of the nuclear fuel when this is used during operation. The amount of such gases, fission gases, outside the nuclear fuel element is accordingly reduced during normal op-

eration conditions thanks to the increased grain size of the nuclear fuel.

It may also be assumed that an increased corrosion resistance results from an increased grain size of the nuclear fuel, since corrosion preferably starts at the grain boundaries and the relationship between the total grain boundary area and the volume of a nuclear fuel element is reduced, i.e. the total grain boundary area is reduced, when the grain size increases. A good corrosion resistance is desired, since the nuclear fuel may come into contact with steam or water during the operation as consequence of damage on a surrounding cladding tube. Corrosion products may then be spread further out in the plant, which should be avoided for reasons known per se.

Besides the fact that the additions mentioned above result in a larger grain size of the nuclear fuel and the advantages associated therewith, at least some of them contribute to an increase of the density of the nuclear fuel element, with respect to the weight of the very nuclear fuel, for example U, Th or Pu, in relation to the volume of the nuclear fuel element. Thus, more power may be obtained out of a given volume of the nuclear fuel.

At least some of said additions also result in an increase of the plasticity of the nuclear fuel element sintered. This results in a smaller risk of damage on surrounding cladding tubes at rapid power increases during operation, and volume changes of the nuclear fuel element associated therewith, since the fuel element with less power than otherwise acts on the cladding tube.

Cr_2O_3 is the addition of those mentioned above that gives the mostly noticeable result. The prior art uses therefor preferably Cr_2O_3 for obtaining the effects mentioned above, primarily the increase of the grain size of the nuclear fuel. However, Cr_2O_3 has to be considered as a poison in this context, since Cr has a comparatively large neutron absorption cross section, which in

its turn may have a negative influence upon the power of the nuclear fuel element, which has been understood by the applicant. According to the prior art 1000-5000 ppm Cr is added (separate or as Cr_2O_3) with respect to the amount of the nuclear fuel with oxide base, for example UO_2 , for obtaining the effects mentioned above.

SUMMARY OF THE INVENTION

10 An object of the present invention is to provide a method which ~~benefits by the effects obtainable through addition of a further oxide,~~ preferably chrome oxide to the nuclear fuel with oxide base at the same time as the amount of chrome oxide added is regulated while considering the negative consequences of the
15 presence of Cr in the nuclear fuel element.

The method defined in the introduction is for obtaining this object characterized in that the amount Cr added is ≥ 50 ppm and < 1000 ppm with respect to the amount of nuclear fuel with oxide base added. Such amounts of added chrome oxide result in
20 remarkably increased grain sizes of different nuclear fuels with oxide base, such as UO_2 in connection with the sintering of the nuclear fuel element, at the same time as the amount Cr is kept at a lower level than before, and has accordingly a reduced
25 negative influence upon the efficiency of the nuclear fuel element during operation, in spite of the comparatively high neutron absorption cross section thereof. A still more preferred interval with respect to the amount of Cr is 100-700 ppm.

30 According to a preferred embodiment of the method a powder comprising at least one further metal oxide is also added, the metal of which has a substantially smaller neutron absorption cross section than Cr, to such an amount that it contributes noticeably to a grain enlarging effect of the chrome oxide upon the
35 nuclear fuel at the sintering. The further metal oxide is preferably any of Nb_2O_5 , Al_2O_3 and MgO . Said additions are alone or in

combination with each other insufficient for obtaining the effects obtained by the chrome oxide, but they function excellent as supplements to the chrome oxide. The chrome oxide is preferably Cr_2O_3 .

According to a further preferred embodiment of the method the further metal oxide comprises Al_2O_3 and the amount of Al added is ≥ 20 , and preferably ≤ 300 ppm. Below 20 ppm the effect of Al_2O_3 added is rapidly reduced. Above 300 ppm the further positive effects of Al_2O_3 get marginal with the chrome oxide proportion in question.

According to a further preferred embodiment of the method the further metal oxide comprises MgO, in which the amount of Mg added is ≥ 20 , and preferably ≤ 300 ppm. Below 20 ppm the positive effects of MgO upon the nuclear fuel with oxide base are reduced rapidly. Above 300 ppm Mg the further positive effects of MgO gets marginal with the chrome oxide proportion in question.

A further object of the invention is to provide a material with oxide base adapted to be sintered to a nuclear fuel element, which through a content of chrome oxide determined in advance and as a result of the composition thereof gets the advantages in the form of higher density, larger nuclear fuel grains and better plasticity resulting from the additions of said further oxides mentioned in the introduction, at the same time as a neutron absorption cross section being as low as possible is obtained for the nuclear fuel element.

This object is obtained by means of a material of the type defined in the introduction, which is characterized in that the amount Cr is ≥ 50 ppm and < 1000 ppm with respect to the amount of nuclear fuel with oxide base.

According to a preferred embodiment the material with oxide base comprises also at least one further metal oxide, the metal of which has a substantially smaller neutron absorption cross section than Cr and is present in such an amount that it contributes noticeably to the grain enlarging effect of the chrome oxide upon the nuclear fuel with oxide base at a sintering of the material. A further metal oxide may be any of Nb_2O_5 , Al_2O_3 and MgO already mentioned. Presence of several of these oxides jointly is also possible in the material. The further metal oxide or oxides has a supplementary object with respect to the chrome oxide, without increasing the total neutron absorption cross section of the nuclear fuel element noticeably.

According to a further preferred embodiment said metal oxide comprises aluminium oxide in the form of Al_2O_3 , in which the amount is ≥ 20 , and preferably ≤ 300 ppm with respect to the amount nuclear fuel. Below 20 ppm the effects of Al_2O_3 added are reduced. Above 300 ppm Al the further positive effects of Al_2O_3 gets marginal with the chrome oxide proportion in question.

According to a further preferred embodiment the metal oxide comprises magnesium oxide in the form of MgO , in which the amount Mg is ≥ 20 , and preferably ≤ 300 ppm with respect to the amount nuclear fuel. The amount MgO is restricted for the same reasons as for Al_2O_3 .

Further advantages and features of the method and the material according to the invention will appear from the detailed description following and the other dependent claims.

DETAILED DESCRIPTION OF AN EMBODIMENT

According to a preferred embodiment of the method according to the invention one or a plurality of powders comprising Cr_2O_3 ,

Al_2O_3 and MgO is added to a powder comprising a nuclear fuel with oxide base, in this case UO_2 .

5 The amount Cr_2O_3 added, where Cr is in the interval 50-1000 ppm (weight proportions with respect to the weight of UO_2), the amount Al added in the form of Al_2O_3 is in the interval 20-300 ppm and the amount Mg added in the form of MgO is in the interval 20-300 ppm. An adhesive and a lubricant are added separately or as a part of any of said powders as already known per se.
10

The powders are then mixed in any way known per se so that a homogenous mixture is obtained.

15 The homogenous powder mixture is then pressed into one or several green bodies, by a pressure of 200-700 MPa.

The green body or bodies is after that sintered in a hydrogen atmosphere with an addition of 0,1-5,0 % of CO_2 , as an alternative only in humidified hydrogen without an addition of CO_2 . The sintering lasts for 1-6 hours at a temperature of 1400-1800°C and under atmosphere pressure. A density very close to the theoretical density is obtained thereby. The UO_2 grains, which at the beginning had a grain size in the order of 10 μm , have during the sintering grown to $\geq 25 \mu\text{m}$, i.e. they have become considerably larger.
20
25

The oxides Cr_2O_3 , Al_2O_3 and MgO added have during the sintering formed a liquid phase which in the material sintered and cooled, i.e. the fuel element formed, forms the matrix around the UO_2 -particles present in the sintered body.
30

Variations of the preferred embodiment described will of course be apparent to a man skilled in the art, but he will then not go around the scope of protection defined by the appended claims with support by the description of the invention.
35

5 The method and the material according to the invention are well suited for production of nuclear fuel elements in the form of fuel pellets, which are positioned in cladding tubes and are used in compressed-water reactors and boiling water reactors for extraction of nuclear energy through nuclear fission activated by neutron irradiation.

10 It has to be pointed out that the ppm values mentioned relate to weight metal/weight nuclear fuel with oxide base, for example weight Cr/weight UO_2 .

CLAIMS:

1. A method for production of a nuclear fuel element with oxide base, in which the nuclear fuel with oxide base is mixed with chrome oxide and sintered to a solid body, characterized in that Cr is added to the nuclear fuel with oxide base at a portion of ≥ 50 ppm and < 1000 ppm with respect to the amount of nuclear fuel with oxide base.
2. A method according to claim 1, characterized in that at least one further metal oxide, the metal of which has a substantially smaller neutron absorption cross section than Cr, is added at such an amount that it will contribute noticeably to a grain enlarging effect of chrome oxide on the nuclear fuel in the sintering.
3. A method according to claim 1 or 2, characterized in that the chrome oxide is Cr_2O_3 .
4. A method according to claim 2 or 3, characterized in that the further metal oxide comprises aluminium oxide.
5. A method according to claim 4, characterized in that the aluminium oxide comprises Al_2O_3 and that the amount of Al added is ≥ 20 , and preferably ≤ 300 ppm.
6. A method according to any of claims 2-5, characterized in that the further metal oxide comprises magnesium oxide.
7. A method according to claim 6, characterized in that the magnesium oxide comprises MgO and the amount Mg added is ≥ 20 , and preferably ≤ 300 ppm.
8. A method according to any of claims 1-7, characterized in that the sintering is carried out at a temperature at which the chrome oxide and the possibly further metal oxide form a liq-

uid phase which after the sintering forms a matrix between particles of the nuclear fuel with oxide base.

- 5 9. A method according to any of claims 1-8, characterized in that the nuclear fuel with oxide base comprises at least one of the oxides UO_2 , ThO_2 and PuO_2 .
- 10 10. A material with oxide base adapted to be sintered to a nuclear fuel element, which comprises a nuclear fuel with oxide base and chrome oxide, characterized in that the amount Cr is ≥ 50 ppm and ≤ 1000 ppm with respect to the amount of the nuclear fuel with oxide base.
- 15 11. A material with oxide base according to claim 10, characterized in that it comprises at least one further metal oxide, the metal of which has a substantially smaller neutron absorption cross section than Cr and is present in such an amount that it contributes noticeably to a grain enlarging effect of chrome oxide upon the nuclear fuel with oxide base at the sintering
20 of the material.
12. A material with oxide base according to claim 10 or 11, characterized in that the chrome oxide is Cr_2O_3 .
- 25 13. A material with oxide base according to claim 11 or 12, characterized in that the further metal oxide comprises aluminium oxide.
- 30 14. A material with oxide base according to claim 13, characterized in that the aluminium oxide is Al_2O_3 and that the amount Al is ≥ 20 , and preferably ≤ 300 ppm.
- 35 15. A material with oxide base according to any of claims 11-14, characterized in that the further metal oxide comprises magnesium oxide.

16. A material with oxide base according to claim 15, characterized in that the magnesium oxide is MgO and that the amount Mg is ≥ 20 , and preferably ≤ 300 ppm.
- 5 17. A material with oxide base according to any of claims 10-16, characterized in that the nuclear fuel with oxide base comprises at least one of UO_2 , ThO_2 and PuO_2 .

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 00/00237

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: G21C 3/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9706535 A1 (BRITISH NUCLEAR FUELS PLC), 20 February 1997 (20.02.97), page 3, line 7 - line 13; page 6, line 26 - page 7, line 25; page 9, line 1 - line 6 --	1-17
X	GB 1334391 A (BELGONUCLEAIRE S.A.), 17 October 1973 (17.10.73), page 1, line 62 - page 2, line 16 --	1-17
A	DE 19627806 A1 (SIEMENS AG), 15 January 1998 (15.01.98), abstract -- -----	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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